77-869
J. Nelson

International Biodeterioration Bulletin ISSN 0020-6164 18(1) Spring 1982

THE EFFECTS OF METALS UPON THE INHIBITORY ACTIVITIES OF CUTTING FLUID PRESERVATIVES

E. O. Bennett[1], J. E. Gannon[1] and I. U. Onyekwelu[1]

Summary

The effects of 15 different metals upon the inhibitory properties of 12 cutting fluid preservatives were studied. Thirteen metals increased the inhibitory properties of Grotan HD II while four improved the action of Ucarcide 250. The other metals had no deleterious effect upon the two inhibitors.

Kathon 886 and Proxel CRL produced mixed results with a few metals improving theier inhibitory properties or having no significant effect, while the bulk of the metals reduced the activities of the compounds.

Les effects des métaux sur l'action inhibitrice des produits de préservation des liquides de coupe

On a étudié les effets de 15 métaux différents sur les propriétés inhibitrices de 12 produits de préservation des liquids de coupes. Treize métaux ont augmenté les propriétés inhibitrices du Grotan HD II alors que quatre ont amélioré l'action de l'Ucarcide 250. Les autres métaux n'ont pas eu d'effet délétère sur les deux inhibiteurs.

Le Kathon 886 et le Proxel CRL ont donné des résultats mixtes avec quelques métaux, améliorant leurs propriétés inhibitrices ou n'ayant pas d'effet significatif alors que le gros des métaux a réduit l'activité des composés.

Der Einfluß von Metallen auf die hemmenden Eigenschaften von Schutzmitteln für Kuhl- und Schmierstoffe

Die Wirkung von 15 verschiedenen Metallen auf die hemmenden Eigenschaften von Schutzmitteln fur Schneidflussigkeiten wurde untersucht. Dreizehn Metalle erhohten die hemmenden Eigenschaften von Grotan HD II, wahrend vier die Wirkungsweise von Ucarcide 250 verstarkten. Die anderen Metalle hatten keinen schadlichen Einfluß auf die zwei Schutzmittel.

Kathon 886 und Proxel CRL ergaben unterschiedliche Ergebnisse, wobei einige Metalle die hemmenden Eigenschaften verbesserten oder keine ausgeprägte Wirkung zeigten, während der größte Teil der Metalle die Wirksamkeit dieser Verbindungen verringerte.

El Efecto de Metales Sobre la Actividad Inhibitoria de Liquidos Lubricantes Antisepticos

Se han estudiado el efecto de 15 metales diferentes sobre las propiedades inhibitorias de 12 liquidos lubricantes. Trece metales incrementan las propiedades inhibitorias del Grotan HD II mientras 4 mejoran la acción del Ucarcide 250. Los otros metales no tienen ningun efecto sobre 2 inhibidores el Kathon 886 y Proxel CRL produjeron resultados mezclados con unos pocos metales mejorando sus propiedades inhibitorias o no teniendo efecto significante mientras que la mayoria de los metales redujeron la actividad de los compuestos.

Introduction

In view of the fact that metals are the major contaminants of working cutting fluids, it is surprising that there are few studies in the literature pertaining to the effects of these materials on rancidity control. Iron chips have been added to test systems employed to study the efficacy of various antimicrobial agents (Pivnick and Fabian, 1953; Wheeler and Bennett, 1956; Kitzke and McGray, 1959; Flemming and Baker, 1959; Himmelfarb and Scott, 1968; Rossmoore and Williams, 1971; Rogers, Kaplan and Beaumont, 1975). These studies did not employ the preservative both in the presence and absence of the metal in order to detect the effect of the metal itself upon preservative action.

There is only one report pertaining to the effect of metals upon the efficacy of cutting fluid preservatives (Bennett, 1973). This study involved only 5 metals and demonstrated that iron, aluminium, zinc, magnesium and copper could influence preservative action.

The objective of this present investigation was to study the effects of most metals involved in machining operations, both in the pure form as well as in alloy, upon preservative action in a representative number of cutting fluids.

Experimental procedure

The test units consisted of wide mouthed glass containers of sufficient size to hold approximately 1 litre of liquid. Each unit was aerated at all times by employing a capillary pipette. The amount of aeration was controlled by a valve so that uniform "rolling" of the coolant was obtained in the units.

Five hundred ml of tap water (approximately 120 ppm hardness), the desired concentration of preservative (wt/vol or vol/vol) and 1.0 g of a metal was added to the appropriate test unit. The metals employed in the study were purchased from chemical supply houses and were of purified quality. Each was in powder form except titanium which was in the form of a sponge.

The coolant concentrate was added (15.0 ml) and thoroughly mixed until a uniform emulsion was formed. The coolant was diluted to 600.0 ml by adding additional tap water and the liquid level was carefully marked upon the container. Once each week, distilled water was added to bring the liquid level back to this mark. Distilled water was used in order to avoid a build-up of organic salts over a period of time.

The units were inoculated with 1.0 ml each of a bacterial inoculum and a mould inoculum, and

52 54 66 79 93

[1] Department of Biology, University of Houston, Houston, Texas, 77004, USA

(Received, September 1981)

90 TX

reinoculated once a each week with a 1.0 ml of a 50/50 mixture of the two inocula. The organisms in the inocula originally came from spoiled samples of industrial cutting fluids. The bacterial inoculum, while subject to some variation, consisted predominantly of different species of pseudomonads with lesser numbers of *Paracolobacterium*, *Proteus*, and *Klebsiella* species. The mould culture consisted mostly of *Fusarium* and *Cephalosporium* species with minor numbers of *Candida* and *Monilia*. The bacterial inoculum was maintained in a petroleum based cutting fluid known to be highly susceptible to bacterial attack and was aerated at all times.

The mould inoculum was maintained in a synthetic coolant known to be highly susceptible to slime formation under constant aeration. Each week the containers were shaken vigorously and approximately three-fourths of the coolant removed and fresh fluid added in order to maintain vigorous growth. Neither of the two inocula have been grown on any substrate other than cutting fluids for several years. The bacterial inoculum contained between 25 and 100 million cells per ml while the mould culture contained between 100,000 and 250,000 units/ml.

Once each week, each unit was examined for its microbial content using standard microbiological procedures designed to enumerate bacteria and moulds. Subculture media were incubated at 35°C and read after 48 hours. Test were continued until two consecutive counts in excess of 100,000 organisms per ml were obtained or until visible slime formed in the units. All units which contained less than 100,000 organisms/ml or did not develop slime were studied for 105 days.

Every effort was made to provide maximum challenge to the chemicals employed to treat the coolants. All units were open to aerial contamination, no effort was made to prevent introduction of organisms via the compressed air and the water used to dilute the coolants was not sterilized. These conditions simulated, as far as possible, those encountered under industrial usage.

All counts, inoculations, subculturing, make-up, and any other practice was done at the same time each week in order to minimize any variation in results from this source. All experiments were done in duplicate and where the data are of significant importance, experiments were repeated a number of times.

Since this investigation constitutes a continuation of previous investigations pertaining to antimicrobial agents in cutting fluids, additional controls were included. These consisted of four units containing a common cutting fluid preservative (Milidin TI-10) in a petroleum base product (Shell Dromus B). These controls are kept under test at all times; they fail in 21 to 28 days due to mould growth and have done so for several years. These contr ls functioned normally during the test period.

Preservatives employed

The preservatives employed in this investigation included the following products. Each was used at a concentration of 1000 ppm except Kathon 886 which was used at a level of 100 ppm. Throughout, the concentrations stated are those of the products as received; they are *not* the concentration of the active ingredients.

Dowicide A
A 97% active powder of sodium o-phenyl-phenate produced by the Dow Chemical Company, Midland, Mich., USA.

Tris Nitro
A 50% solution of tris (hydroxymethyl)-nitromethane produced by the IMC Chemical Group, Des Plaines, Ill., USA.

Grotan
A 78.5% solution of hexahydro-1, 3, 5-tris (2-hydroxyethyl)-s-triazine produced by the Lehn and Fink Industrial Products Division of Sterling Drug, Inc., Montvale, N. J., USA.

Milidin TI-10
A solution (concentration not given) of hexahydro-1,3,5 -tris (2-hydroxyethyl)-s-triazine-iodine complex produced by the DeMille Chemical Corp., Jersey City, N. J., USA.

Vancide TH
A 95% solution of hexahydro-1, 3, 5-triethyl-s-triazine produced by the R. T. Vanderbilt Co. Inc., New York, N. Y., USA.

Dowicil 75
A 67.5% active powder of 1-(3-chloroallyl)-3, 5, 7-triaza-1-azoniaadamantane chloride produced by the Dow Chemical Company, Midland, Mich., USA.

Bioban P-1487
A solution containing 70% 4-(2-nitrobutyl) morpholine and 20% 4, 4-(2-ethyl-2-nitromethylene) dimorpholine produced by IMC Chemical Group, Des Plaines, Ill., USA.

Sodium Omadine
A 40% solution of sodium pyridine thiol-1-oxide produced by the Olin Corp., Stamford, Conn., USA.

Proxel CRL
A 30% solution of 1, 2-benziosothiazolin-3-one produced by ICI United States Inc., Wilmington, Del., USA.

Kathon 886
A solution containing 8.6% of 5-chloro-2-methyl-4-isothiazolin-3-one and 2.6% 2-methyl-4-isothiazolin-3-one and 2.6% 2-methyl-4-isothiazolin-3-one produced by Rohm and Haas Company, Philadelphia, Pa., USA.

Grotan HD II
A powder containing 2-chloro-N-(hydroxymethyl)-acetamide (39%), sodium tetraborate (41%), potassium iodide (0.39%), produced by the Lehn and Fink Industrial Products Division of Sterling Drugs, Inc., Montvale, N. J., USA.

Ucarcide 250
A 50% solution of gluteraldehyde produced by Union Carbide Corp., New York, N. Y., USA.

Cutting fluids employed

Irmco 310 (emulsion) International Refining and Manufacturing Co., Evanston, Ill., USA.

Shamrock (synthetic) F. E. Anderson Oil and Chemical Co., Portland, Conn., USA.

Dascool (emulsion) D. A. Stuart Oil Co., Scarborough, Ont., Canada.

Sanson 7080NB (emulsion) Henry E. Sanson & Sons, Inc., Bristol, Pa., USA.

Quaker 18A (synthetic) Quaker Chemical Corp., Conshohocken, Penn., USA.

Results

The results of this investigation are presented in Tables 1, 2 and 3. Only two preservatives, Grotan HD II and Ucarcide 250, were not adversely affected by metals. More importantly, the anti-microbial properties of Grotan HD II were significantly increased in the presence of all but two of the metals. It may be noted that those preservatives which are generally known as formaldehyde releasers were almost uniformly adversely affected by metals.

The patterns produced by the individual metals are of interest. For example, iron produced no significant effect upon the inhibitory properties of Grotan HD II, Urcacide 250, or Kathon 886, but adversely affected the action of all the other preservatives. Molybdenum improved inhibition in Grotan HD II, Urcacide and Kathon 886; it had no significant effect upon Proxel CRL, Tris Nitro, or Bioban P-1487 and produced a deleterious effect upon other preservatives.

Statistical studies were conducted to determine if valance(s), molecular weights, or other factors influenced the specific effects. No correlation with any other factor could be established. Even closely related preservatives such as Grotan and Milidin TI-10 exhibited quite different results with the same metal.

Discussion

It has been known for many years that the presence of iron increases the oxidation of hydrocarbons (Zuidema, 1946) and reduces the working lives of cutting fluids (Flemming & Baker, 1959). It also has been noted that the presence of iron, magnesium or aluminium ions decreases the useful lives of rolling oils (Tripathi, 1975). In regards to iron, the sulphur content of the fines may be the most important factor in deterioration. Fines containing no more than 0.1% sulphur caused practically no spoilage while fines containing higher levels of sulphur caused emulsions to spoil in a short time.

Metallic ions influence deterioration in several ways. First, metallic ions can stimulate microbial growth (Zuidema, 1946; Englander and Corden, 1971) particularly in an alkaline environment. Second, there are numerous references in the literature concerning the well established fact that metals can influence the action of antimicrobial agents (Weinberg, 1957).

The results of this investigation show that metals generally interfere with the action of most cutting fluid preservatives. In certain instances, they can improve the inhibitory properties of a few preservatives.

The results show that Grotan HD II and Ucarcide 250 would be the preservatives most likely to control rancidity particularly in situations where the coolant becomes heavily loaded with fines. It must be remembered that none of the preservatives currently available are effective in all products. The tables can be

Table 1

Effects of Metals on the Inhibitory Properties of Cutting Fluid Preservatives

% increase in activity in presence of 1.0g of metal in 500ml

METAL	GROTAN HD II	UCARCIDE 250
Copper	74.6	76.1
Molybdenum	80.0	58.1
Magnesium	56.8	20.5
Zinc	30.9	41.0
Cobalt	47.7	*
Aluminium	38.3	*
Manganese	38.3	*
Cadmium	33.6	*
Titanium	33.6	*
Nickel	30.9	*
Tin	30.9	*
Lead	30.9	*
Tungsten	24.8	*
Iron	*	*
Chromium	*	*

* N significant difference from control containing no metal.

Results represent means of duplicate determination with 5 different cutting fluids diluted 1-40.

Table 2

Effects of Metals on the Inhibitory Properties of Cutting Fluid Preservatives

% increase (+) or decrease (-) in activity in presence of 1.0g of metal in 500ml

METAL	KATHON 886	O-PHENYL PHENATE	PROXEL CRL	SODIUM OMADINE
Copper	+30.1	+22.0	*	-82.1
Magnesium	-50.0	-46.9	+30.7	-53.4
Zinc	-42.2	-57.6	*	-89.3
Cadmium	+23.5	-53.2	+46.8	-39.0
Iron	*	-56.3	-22.4	-89.3
Nickel	-55.2	-56.3	-42.4	-74.9
Cobalt	*	-56.3	-40.1	-80.6
Tin	-30.8	-46.9	-31.3	-49.8
Lead	+33	*	*	+55.8
Aluminium	-45.7	-53.2	*	-53.4
Titanium	-26.4	-46.9	-33.5	-60.6
Chromium	-18.5	-53.2	-33.5	-74.9
Manganese	*	-65.7	-18.0	-56.0
Molybdenum	+20.2	-84.4	*	-85.7
Tungsten	-17.2	-77.2	-24.6	-46.2

* No significant difference from control containing no metal.

Results represent means of duplicate determinations with 5 different cutting fluids diluted 1-40.

Table 3

Effects of Metals on the Inhibitory Properties of Cutting Fluid Preservatives

% decrease in activity in presence of 1.0g of metal in 500ml

METAL TH75	GROTAN P-1487	TRIS NITRO	MILIDIN TI-10	VANCIDE	DOWICIL	BIOBAN
Copper	69.2	33.9	60.5	27.8	68.9	24.8
Magnesium	40.6	44.3	54.8	29.7	36.3	58.3
Zinc	73.9	68.7	37.8	46.3	57.8	70.8
Cadmium	59.6	16.5	*	31.5	40.0	26.2
Iron	71.5	86.1	58.6	29.7	24.5	62.4
Nickel	54.9	33.9	20.9	22.3	44.5	24.8
Cobalt	23.7	59.3	60.5	30.8	51.2	55.5
Tin	47.8	68.7	*	24.7	51.2	38.8
Lead	*	61.7	*	*	22.3	66.6
Aluminium	66.8	30.4	37.8	48.2	77.8	*
Titanium	71.1	23.4	18.0	24.1	42.3	45.7
Chromium	45.2	23.4	*	29.7	40.0	44.3
Manganese	76.3	64.7	57.6	37.1	46.7	66.6
Molybdenum	59.6	*	26.5	53.8	37.8	*
Tungsten	28.7	40.8	71.8	27.8	31.2	55.5

used to select the preservative which is least affected by the metal being worked. For example, if an individual required a preservative for a coolant used to machine magnesium and it was found that Grotan HD II or Ucarcide 250 were ineffective in the product, then the tables show that Proxel CRL would possibly be the preservative to consider for use. In some instances, the individual might have to select a preservative which is least adversely affected by the metal being worked.

It has been reported that magnesium ions increased the inhibitory properties of glutaraldehyde (Ucarcide 250) (Gorman and Scott, 1979) and this was noted in this investigation. The effects of metals upon the action of phenolics has been reviewed (Bennett, 1959), and it was noted that copper increases the action of these preservatives, and this too has been observed in the study. Cobalt has been reported to increase the inhibitory action of phenolics; however, this was not noted in this investigation.

An additional factor of interest is that it has been found that Grotan HD II exhibits about a four fold increase in activity when employed with EDTA. If metals increase the inhibitory properties of this preservative, then their removal via the use of a chelating agent should neutralise the effect.

Experiments employing Grotan HD II with EDTA and Grotan HD II with metals were repeated a number of times and both potentiate the inhibitory properties of the preservative. It is likely that the mode of action of Grotan HD II and metals is different than that of the preservative and EDTA upon the cells.

The results open for further consideration, the practice of using iron fines in laboratory tests to establish the efficacy of a chemical as a cutting fluid preservative. Since iron had generally a negative effect upon preservative action, the presence of this metal in routine screening tests could eliminate chemicals which might be favourably affected by other metals.

In the development of a new cutting fluid preservative, it appears advisable to study the effects of metals upon the compound but these test should follow those which indicate general activity in these products. In order to reduce developmental costs, it would be fortunate if a standard mixture of metallic powders could be developed for such tests in order to avoid studying each metal individually.

It should be noted that it may be possible to improve the antimicrobial properties of certain cutting fluid preservatives by adding small concentrations of metallic salts to the products. For example, a copper salt might increase the antimicrobial properties of Gr tan HD II, Ucarcide 250 and Kathon 886.

References

Bennett, E. O. (1959)
Factors affecting the antimicrobial activity of phenol.
Advan. Appl. Microbiol. 1: 123-7.

Bennett E. O. (1973)
Microbiological aspects of metalworking fluids.
S. M. E. Technical Paper No. MR73-826; 1-127.

Englander, C. M. and Corden, M. E. (1971)
Stimulation of mycelial growth of *Endothia parastica* by heavy metals.
Appl. Microbiol., 22: 1012-1016.

Fleming, C. D. and Baker, R. J. (1959)
Controlling the spoilage of water soluble cutting fluids.
Paper presented at the 14th ASLE annual meeting, Buffalo, N. Y., Preprint No. 59AM 3A-2.

Gorman, S. P. and Scott, E. M. (1979)
Effect of inorganic cations on the biocidal and cellular activity of gluteraldehyde.
J. Appl. Bact., 47: 463-468.

Himmelfarb, P. and Scott, A. (1968)
Simple circulating tank test for evaulation of germicides in cutting fluid emulsions.
Appl. Microbiol., 16: 1437-1438.

Kitzke, E. D. and McGray, R. J. (1959)
Coolant microbiology: the role of industrial research.
Paper presented to the 14th ASLE national meeting, Buffalo, N. Y., Paper No. 59AM 3A-/

Onyekwelu, I. U., Bennett, E. O. and Gannon, J. E. (1981)
The effective life of preservatives in cutting fluid concentrates
Tribiology International, 14: 7-9.

Pivnick, H. and Fabian, F. W. (1953)
Methods for testing the germicidal value of chemical compounds for disinfecting soluble oil emulsions.
Appl. Microbiol., 1: 204-207.

Rogers. M. R., Kaplan, A. M. and Beaumont, E. (1975)
A laboratory in-plant analysis of a test procedure for biocides in metal-working fluids.
Lub. Eng., 31: 301-310.

Rossmoore, H. W. and Williams, B. W. (1971)
An evaluation of a laboratory and plant procedure for preservation of cutting fluids.
International Biodeterioration Bulletin 7: 55-60.

Rossmoore, H. W. and Rossmoore, L. A. (1979)
The identification of a defined microbial inoculum for the evaluation of biocides in water-based metal-working fluids.
ASLE preprint N.79-AM-1A-2: 1-5.

Tripathi, K. C. (1975)
A new method to improve the life and performance of aluminium hot rolling mills.
Aluminium, 51: 574-579.

Weinberg, E. D. (1975)
The mutual effects of antimicrobial compounds and metallic cations.
Bact. Reviews. 21: 46-68.

Wheeler, H. O. and Bennett, E. O. (1956)
Bacterial inhibitors for cutting oil.
Appl. Microbiol., 4: 122-126.

Zuidema, H. H. (1946)
Oxidation of lubricating oils.
Chem. Reviews. 38: 197-226.

ACKNOWLEDGEMENTS

The following companies are acknowledged for their co-operation and financial support which have made this paper possible.

Ab Karlshams Oljefabriker, Sweden; Anderson Oil and Chemical Company, Inc., Portland, Connecticut; Berol Kemi Ab., Sweden; Bellucco & Co., SPA., Torino, Italy; Blaser & Co., AG., Switzerland; Buckeye Lubricants, Bedford, Ohio; Chesson Oil Company, Inc., Lake Charles, Louisiana; D. A. Stuart Oil Company, Chicago, Illinois; DeMille Chemical Corporation, Jersey City, New Jersey; Dober Chemical Corporation, Midlothian, Illinois; Henry E. Sanson & Sons, Inc., Bristol, Pennsylvania; Gunther Schmidt, Hamburg, Germany; IMC Chemical Group, Des Plaines, Illinois; International Chemical Çompany, Philadelphia, Pennsylvania; International Refining & Manufacturing Co., Evanston, Illinois; J. R. Schneider Company Inc., Corte Madera, California; Lehn and Fink Products Company, Montvale, New Jersey; Merck & Company, Inc., Rahway, New Jersey; Metalworking Chemicals & Equipment, Inc., Chester, New Jersey; Monroe Chemical Company, Inc., Hilton, New York; Monsanto Industrial Chemical Company, St Louis, Missouri; Olin Corporation, New Haven, Connecticut; Oil Kraft, Inc., Cincinnati, Ohio; Pillsbury Chemical & Oil, Inc., Detroit, Michigan; Polar Chip, Inc., Irvine, California; Process Research Products, Pennington, New Jersey; Rohm and Haas Company, Philadeplphia, Pennsylvania; S. C. Johnson & Son, Inc., Racine, Wisconsin; S. H. Mack and Company, Inc., St Charles, Illinois; Sinol, Snc., Torino, Italy; TRW., Inc., Jamestown, New York; Tapmatic Corporation, Irvine, California; Tower Oil & Technology Company, Chicago, Illinois; Ry-Chemie Vertriebs-GmbH, Germany; Union Oil Company of California, Brea, California; Van Straaten Chemical Company, Chicago, Illinois.